Machine Translation of DE 10061544

The instant invention concerns a method to the production of soft monodisperse spherical polymers with an average particle size from 2 to 100 mu m as well as the Perl polymers obtained after this method and their uses.

Spherical polymers with an average particle size from 2 to 100 mu m become various applied, z. B. as spacers for film materials, as carriers for catalysts or biological active substances, as calibration substances for light scattering measurements or as starting materials for chromatography resins and ion exchangers. Generally for this polymers with as uniform a particle size as possible become desired (in the following "monodisperse" mentioned).

Homopolymerisate, as for example polymethyl methacrylate, can be produced as Perl polymers with particle sizes from 0,5 to 10 mu m by dispersion polymerization. A suitable method becomes for example 0,610,522 described in EP-A. With the dispersion polymerization a solvent used, are soluble in which the used monomers, however the formed polymer insoluble becomes is. The dispersion polymerization supplies usually high yields of spherical Perl polymers with narrow particle size distribution. However shown has itself that it is difficult larger particles to produce in particular particles with a diameter of more than 7.5 mu m by dispersion polymerization. An other flagstone of the dispersion polymerization is that the particle size distribution with rising particle size becomes broader significant.

Perl polymers with a particle size of approx. 10 to 500 mu m can become on the other hand by suspension polymerization obtained. The bottom one term suspension polymerization becomes a method understood, a monomerhaltiges a mixture, which contains in monomers the soluble initiator, in mixable a phase, essentially not with which a monomer or, with that monomers, which contains a dispersing agent, becomes in the form of droplets, if necessary in the mixture with small, solid particles, divided and by temperature rise bottom agitations cured. Other details of the suspension polymerization become for example in H. Greens "Polymerization Processes", in: Ullmanns Encyclopedia OF Industrial Chemistry, Bd. A21, 5. Aufl. (B. Elvers, S. Hawkins, G. Schulz, Hrsg.), VCH, Weinheim 1992, S. 363-373 described.

A disadvantage of the suspension polymerization is however the broad particle size distribution of the generated Perl polymers. This is in particular very adverse with the use as spacers.

For many applications Perl polymers with better temperature and good become solvent stability desired. These properties are for example of great importance if the Perl polymers as spacers with elevated temperature or in presence of solvent on a substrate applied to become to be supposed. Conventional polymethyl metacrylate Perl polymers or polystyrene of Perl polymers malfunction bottom these conditions.

In the EP-A 0,417,539 becomes the production of temperature and solvent-stable Perl polymers with a particle size of 0,5-10 mu m, preferably 1-7 mu m described, which are crosslinked with SI-O-SI-groups.

The methods of the state of the art to the production of monodisperse Perl polymers relate itself however all together on hard Perl polymers.

Subject-matter of the invention is a method to the production of soft, monodisperse, spherical Perl polymers with an average particle size from 2 to 100 mu m after a seed inlet method, characterised in that one

A) monodisperse, spherical copolymers with a particle size of 1 to 20 mu m as seed in an aqueous continuous phase suspended,
B) to this suspension a mixture from monomers and initiator (inlet), whereby this mixture into the seed in-pours, admits and
C) the poured seed to Perl polymers with elevated temperature polymerized,
whereby the mixture of the inlet

a) 20-85 Gew. - % (Meth) acrylic acid ester with a C4 to C18-Alkylrest
b) 10-50 Gew. - % water-soluble monomer
c) 1-20 Gew. - % crosslinker
d) 0-25 Gew. - % other monomer and
e) 0.05-5 Gew. - % initiator
contains.

The determination of the average particle size (0) and the particle size distribution the image analysis becomes applied. As measure for the width of the particle size distribution of the generated spherical Vinylcopolymerisate the ratio becomes from the 90%-Wert (0 (90)) and the 10%-Wert (0 (10)) the volume distribution of formed. Monodisperse particle size distributions into senses of the instant invention means 0 (90) 0 (10) </= 2.0, prefered 0 (90) /0 (10) </= 1,5.

Monodisperse spherical copolymers with a particle size from 1 to 20 mu m, which are suitable as seed, can become after known methods of the state of the art for example by dispersion polymerization generated. Both uncrosslinked copolymers and crosslinked copolymers are more insertable, if they exhibit a source degree of at least 2.5 (measured with 25 DEG C in ethyl acetate). Suitable copolymers are such from methyl (meth) acrylate and C2 to C18-Alkyl (meth) acrylates. (Meth) acrylate in the sense of the instant invention means both acrylate and methacrylate, equally (Meth) acrylic acid ester stands for methacrylic acid esters and acrylic acid esters.

The monodisperse which can be used prefered in process step A); spherical copolymers exist prefered out

a) 97 to 65 Gew. - %, in particular 95 to 75 Gew. - % methyl (meth) acrylate and
b) 3 to 35 Gew. - %, in particular 5 to 25 Gew. - %, at least (Meth) a acrylic acid ester with a C2 to C18-Alkylrest.

(Meth) of acrylic acid ester with a C2 to C18-Alkylrest in the sense of the invention are the esters of the acrylic acid and methacrylic acid with C2 to C18-Alkoholen. The methacrylic acid esters are prefered. The alkyl radical can be by oxygen atoms interrupted. Prefered ones are C6 to C18-Ester von Methacrylsäure. Mentioned ethyl methacrylate, n-propyl methacrylate, ISO propyl methacrylate, n Butylmethacrylat, ISO Butylmethacrylat, n-Hexylmethacrylat, 2-Ethylhexylmethacrylat, n-Octylmethacrylat, n-Decyhnethacrylat, Methoxyethylmethacrylat, Methoxybutylmethacrylat, Triethylenglycolmonomethacrylat, n-Dodecylmethacrylat, Tridecylmethacrylat or Stearylmethacrylat is exemplary.

According to invention the spherical copolymer which can be used in process step A) possesses an average particle size from 1 to 20 mu m, preferably 1 to 12 mu m, particularly prefered 2 to 10 mu M.

The seed which can be used in the process step A) becomes suspended in an aqueous, continuous phase, whereby the ratio of seed and water is to a large extent uncritical. It can for example between 1: 1 and 1: 100, preferably between 1: 2 and 1: 10 lies. Suspending can take place for example with the help of a normal lattice or sheet agitator, whereby low to middle shear forces applied become.

In the process step B) an inlet becomes from monomer and initiator added the suspended seed polymer.

The inlet contains 20-85 Gew. - %, preferably 30-80 Gew. - % (Meth) acrylic acid ester with a C4 to C18-Alkylrest (A). According to invention prefered (Meth) acrylic acid esters (A) are listed already with the characterization of the seed copolymer above.

The amount of the water-soluble monomer (B) amounts to 10-50 Gew. - %, prefered 10-30 Gew. - % related to the inlet. Water-soluble monomers (B) in the sense of the instant invention are monoethylenic unsaturated compounds, itself with 20 DEG C to more than 5 Gew. - % in waters solve. As examples are mentioned: Acrylic acid and their alkali and ammonium salts, methacrylic acid and their alkali and ammonium salts, hydroxyethyl methacrylate, hydroxyethyl acrylate, Diethylenglykolmonoacrylat, Diethylenglykolmonomethacrylat, tri ethyl glycol mono acrylate, Triethylenglykolmonomethacrylat, Tetraethylenglykohnonoacrylat, Tetraethylenglykolmonomethacrylat, Glycerinmonoacrylat, Aminoethylinethacrylat, dimethylaminoethyl methacrylate, acrylamide, methacrylamide, vinyl pyrrolidone or vinylimidazole. Prefered one is hydroxyethyl methacrylate.

The crosslinker (C) becomes in amounts of 1-20 Gew. - %, prefered 2-10 Gew. - % related to the inlet used. Crosslinkers (C) in the sense of the instant invention are compounds with at least two ethylenic unsaturated groups in the molecule, as for example allyl methacrylate, ethylene glycol dimethacrylate, Ethylenglykoldiacrylat, Butandioldiacrylat, Butandioldimethacrylat, Hexandioldimethacrylat, Triethylenglykoldimethacrylat, Tetraethylenglykoldimethacrylat, trimethylolpropane triacrylate, Pentaerythritoltetramethacrylat or divinylbenzene. Prefered one is ethylene glycol dimethacrylate.

In the sense of the instant invention become as other monomers D), for example styrene, alpha - methyl styrenes, vinyl chloride, vinylidene chloride, vinyl acetate, vinyl propionate, Vinyllaurat, Vinyladipat, methyl methacrylate, methyl acrylate, ethyl acrylate, Isopropylmethacrylat, n-propyl methacrylate or acrylonitriles in amounts of 0-25 Gew. - %, preferably 0-10 Gew. - % used.

As initiators all substances usually useful for the introduction of polymerizations can become used at the time of the execution of the invention process. Preferably in considerations oil-soluble initiators come. Exemplarily mentioned is peroxy compounds, like Dibenzoylperoxid, Dilauroylperoxid, to (p-chlorbenzoylperoxid), Dicyclohexylperoxidicarbonat, third. - Butylperoctoat, 2,5-Bis (2-ethylhexanoylperoxi) - 2,5-dimethylhexan or third. - Amylperoxy-2-ethylhexan, as well as azo compounds, like 2,2 ' - Azobis (isobutyronitril), 2,2 - Azobis (2,4-dimethylvaleronitril), 2,2 ' - Azobis (2-methylisobutyronitril), 2,2 ' - Azobis [2 (2-imidazolin-2-yl) propane] or 2,2 ' - Azobis (2-amidinopropane) dihydrochlorid.

The inlet can contain beyond that if necessary molecular weight automatic controllers for example of dodecyl mercaptans, Butylmercaptan or mercaptoethanols.

In order to obtain and suppress around an undesirable polymerization of the inlet in the water phase high yields, the water phase water-soluble radical scavengers can become added if necessary. As Radialfänger, often also as inhibitors referred, come both inorganic and organic into question. Examples for inorganic inhibitors are nitrogen compounds such as hydroxylamine, hydrazine, sodium nitrite and Kaliumnitrit. Examples for organic inhibitors are phenolic compounds such as hydroquinones, Hydrochinonmonomethylether, resorcinol, pyrocatechol and third. - Butylbrenzkatechin. Also condensed phenols, as [(3,3 ', 3 ', 5,5 ', 5 ' - hexadecimal third butyl A, a', a' (mesitylene-2,4,6-triyl) trichloroethylene p-cresol] are favourable. Other organic inhibitors are for example nitrogen containing compounds such as Diethylhydroxylamin or Isopropylhydroxylamin. The concentration of the inhibitor which can be used if necessary amounts to 5-1000 ppm, preferably 10-500 ppm, particularly prefered 20-250 ppm, related to the aqueous phase.

In a preferable embodiment of the seed inlet method according to invention this in presence of a dispersing agent conducted becomes. As dispersing agents all come usually for this purpose substances which can be used into considerations. Preferably mentioned is natural or synthetic water-soluble polymers, like gelatin, starch or cellulose derivatives, in particular cellulose esters or cellulose ethers, furthermore polyvinyl alcohol, polyvinylpyrrolidone, polyacrylic acid, polymethacrylic acid or copolymers from (Meth) acrylic acid or (Meth) acrylic acid esters, and in addition also with alkali metal hydroxide of neutralized copolymers from methacrylic acid or methacrylic acid ester.

In a particular embodiment of the instant invention the inlet becomes added as aqueous emulsion. The emulsion has preferably a phase relationship (o: w) of 1: 2 to 1: 10. The production of the emulsion ionic or nonionic surfactants become used. Examples for nonionic surfactants are the ethoxylated Nonylphenole. As anionic surfactants alkyl sulfonates and the sodium salts of sulfo succinic acid esters are particularly suitable. N-alkyl ammonium salts, as for example Methyltricaprylammoniumchlorid are mentioned as cationic surfactants. Prefered one becomes a combination from ionic and nonionic surfactant, z. B. a mixture from ethoxylated nonylphenols and that sodium salts of the Sulfobernsteinsäurisooctylesters. The surfactant, and/or. the Tensidmischung becomes in an amount from 0,05 to 5 Gew. - %, preferably from 0,1 to 2 Gew. - % related to the inlet used.

The addition of the inlet emulsified if necessary (step B) made for example with room temperature. Normally the inlet becomes added within some hours of the suspended seed.

An also possible so called "dynamic" seed inlet method is to be used. With this process variant the made addition of the inlet with a temperature, is active with which the added initiator, over a longer period, z. B. within 2 to 10 hours.

The introduction of the polymerization (step C) the poured seed becomes heated on a temperature, is active with which the applied initiator. The temperature lies generally between 50 to 100 DEG C, preferably between 75 and 85 DEG C. The polymerization lasts 0.5 h to some hours. After after the polymerization the seed inlet polymer can become particularly favourable from the reaction mixture by filtration or by sedimentation with the help of a centrifuge or a decanter isolated and or several laundries if necessary a dried.

The crosslinking reaction and the finally obtained degree of crosslinking can do analytic in simple manner by the determination of the solubility in a good solvent, for example tetrahydrofurane/an ethyl acetate or a dimethylformamide, followed and/or. controlled become.

In accordance with the invention process one receives soft, monodisperse, spherical Perl polymers with an average particle size from 2 to 100 mu M. The instant invention concerns therefore also soft, monodisperse, spherical Perl polymers with an average particle size from 2 to 100 mu m, available by means of a seed inlet method through

A) Suspend from monodisperse, spherical copolymers with a particle size from 1 to 20 mu m as seed in an aqueous continuous phase,
B) Addition of a mixture from monomers and initiator (Zulau, whereby this mixture in-pours into the seed and
C) Polymerization of the gequollenenen seed to Perl polymers with elevated temperature,
whereby the mixture of the inlet

a) 20-85 Gew. - % (Meth) acrylic acid ester with a C4 to C18-Alkylrest
b) 10-50 Gew. - % water-soluble monomer
c) 1-20 Gew. - % crosslinker
d) 0-25 Gew. - % other monomer and
e) 0.05-5 Gew. - % initiator
contains.

The Perl polymers according to invention are in solvents, as for example acetone, tetrahydrofurane, ethyl acetate, dimethylformamide, methyl ethyl ketone, acetonitrile, insoluble. They are soft and elastic. In addition the Perl polymers according to invention are hydrophilic and can from aqueous dispersion for coating and/or. Modification of surfaces used become.

The soft, monodisperse, spherical Perl polymers prepared in accordance with the invention process can become versatile used beyond that. Prefered own it itself as spacers for film materials, as carriers for catalysts or biological active substances, as calibration substances for light scattering measurements or as starting materials for chromatography resins and ion exchangers.

Example 1

Production of a Perl polymer according to invention

1a) Production of a seed

In one from 210 g methyl methacrylate existing with a lattice agitator equipped 4 litre reactor becomes 2517 g methanol, 180 g polyvinylpyrrolidone (PVP) and 240 g monomer mixture and 30 g ethyl methacrylate an homogeneous solution mixed. Bottom nitrogen is aufgeheitzt this solution within an hour with a stirring rate from 100 rpm to 55 DEG C and with 3 g 2.2 ' - Azobis (isobutyronitril) dissolved in 60 g methyl methacrylate offset. The polymerization mixture becomes other 20 hours with 55 DEG C and 100 rpm agitated. Subsequent one becomes the Perl polymer by sedimentation isolated. The Perl polymers become with methanol and water washed and dried with 70 DEG C in the oven. The particle size of the obtained Perl polymers amounts to 4 mu M.

1b) Production of a Perl polymer by means of seed inlet polymerization

In 4 equipped with a lattice agitator litre reactor becomes 20 g seed from 1a) in 880 g water suspended. The seed suspension becomes a solution from 5 g Walocel 400 PFV ©& (Methylhydroxyethylcellulose, company Wolff Walsrode AG) in 2245 g water added. 12 g Hydroxyethylmethacrylat, 46.2 g ethylhexyl methacrylate, 1.8 g ethylene glycol dimethacrylate, 0.78 g BPO (75%ig) become, 0.86 g Arkopal N60 TM

(Nonylphenolpolyglykolether), 0.08 g aerosol OT TM (Natriumdioctylsulfosuccinat), 0.375 g Irganox 1330 TM [(3.3 ', 3 ', 5.5 ', 5 ' - hexadecimal third butyl A, a', a' (mesitylene-2,4,6-triyl) trichloroethylene p cresol] and 500 g waters with a rotor stator mixer emulsifies. This mixture (inlet) becomes in five steps (23.4 ml in 0,5 ml/min; 115,1 ml in 1,25 ml/min; 207,5 ml in 2,25 ml/min; 115,1 ml in 2,5 ml/min and 136.5 ml in 3 ml/min) to the seed suspension with a metering pump added. The seed becomes cured after 16 h swelling 9 h prolonged with 80 DEG C. The Perl polymer becomes by sedimentation isolated, dried with methanol and water washed and with 70 DEG C. The particle size of the obtained Perl polymers amounts to 6 mu M.

Example 2

Production of a Perl polymer according to invention

2a) Production of a seed

In one from 185 g methyl methacrylate existing with a lattice agitator equipped 4 litre reactor becomes 2517 g methanol, 180 g polyvinylpyrrolidone (PVP) and 240 g monomer mixture and 40 g ethylhexyl methacrylate an homogeneous solution mixed. Bottom nitrogen is aufgeheitzt this solution within an hour with a stirring rate from 100 rpm to 55 DEG C and with 3 g 2.2 ' - Azobis (isobutyronitril) dissolved in 60 g methyl methacrylate offset. The polymerization mixture becomes other 20 hours with 55 DEG C and 100 rpm agitated. Subsequent one becomes the Perl polymer by sedimentation isolated. The Perl polymers become with methanol and water washed and dried with 70 DEG C in the oven. The particle size of the obtained Perl polymers amounts to 6 mu M.

2b) Production of a Perl polymer by means of seed inlet polymerization

In 4 equipped with a lattice agitator litre reactor becomes 20 g seed from example 2a) in 880 g water suspended. The seed suspension becomes a solution from 5 g Walocel 400 PFV TM (Methylhydroxyethylcellulose, company Wolff Walsrode AG) in 2245 g water added. 16 g Hydroxyethylmethacrylat, 61.6 g ethylhexyl methacrylate, 2.4 g ethylene glycol dimethacrylate become, 1.04 g BPO (75%ig), 1.15 g Arkopal N 60 TM (Nonylphenolpolyglykolether), 0.14 g aerosol OT TM (Natriumdioctylsulfosuccinat), 0.5 g Irganox 1330 TM [(3.3 ', 3 ', 5.5 ', 5 ' - hexadecimal third butyl A, a', a' (mesitylene-2,4,6-triyl) trichloroethylene p cresol] and 500 g waters with a rotor stator mixer emulsifies. This mixture (inlet) becomes in five steps (23.4 ml in 0,5 ml/min; 115,1 ml in 1,25 ml/min; 207,5 ml in 2,25 ml/min; 115,1 ml in 2,5 ml/min and 138.5 ml in 3 ml/min) to the seed suspension with a metering pump added. The seed becomes cured after 16 h swelling 9 h prolonged with 80 DEG C. The Perl polymer becomes by sedimentation isolated, dried with methanol and water washed and with 70 DEG C. The particle size of the obtained Perl polymers amounts to 10 mu M.

CLAIMS

1. Method to the production of soft, monodisperse, spherical Perl polymers with an average particle size of 2 to 100 mu m after a seed inlet method characterised in that one

A) monodisperse, spherical copolymers with a particle size of 1 to 20 mu m as seed in an aqueous continuous phase suspended,
B) to this suspension a mixture from monomers and initiator (inlet), whereby this mixture into the seed in-pours, admits and
C) the poured seed to Perl polymers with elevated temperature polymerized, how,
the mixture of the inlet

a) 20-85 Gew. - % (Meth) acrylic acid ester with a C4 to C18-Alkylrest
b) 10-50 Gew. - % water-soluble monomer
c) 1-20 Gew. - % crosslinker and
d) 0-25 Gew. - % other monomer and
e) 0.05-5 Gew. - % initiator
contains.

2. Method to the production of soft, monodisperse, spherical Perl polymers according to claim 1, characterised in that the seed quotients from the 90%-Wert (0 (90)) and the 10%-Wert (0 (10)) the volume distribution of less than 2.0 exhibits.

3. Method according to claim 1, thus identified-draws that this in presence of a molecular weight automatic controller conducted becomes.

4. Method according to claim 1, thus identified-draws that this in presence of inhibitors conducted becomes.

5. Method according to claim 1, characterised in that this in presence of a dispersing agent conducted becomes.

6. Method according to claim 1, characterised in that the inlet as aqueous emulsion added becomes.

7. Soft, monodisperse, spherical Perl polymers with an average particle size of 2 to 100 mu m available by means of seed inlet of a method through

A) Suspend from monodisperse, spherical copolymers with a particle size from 1 to 20 mu m as seed in an

aqueous continuous phase,
B) Addition of a mixture from monomers and initiator (inlet), whereby this mixture in-pours into the seed and
C) Polymerization of the gequollenenen seed to Perl polymers with elevated temperature,
whereby the mixture of the inlet

a) 20-85 Gew. - % (Meth) acrylic acid ester with a C4 to C18-Alkylrest
b) 10-50 Gew. - % water-soluble monomer
c) 1-20 Gew. - % crosslinker
d) 0-25 Gew. - % other monomer and
e) 0,05-5 Gew. - % initiator
contains.

8. Use of the Perl polymers according to claim 7 to the coating or modification of surfaces, as spacers for film materials, as carriers for catalysts or biological active substances, as calibration substances for light scattering measurements or as starting materials for chromatography resins and ion exchangers.